crystal lattices (LS$_2$, LS$_{13}$) by spontaneous crystallization. Velikov *et al.* (*1*) go one step further, illustrating how a new class of binary colloidal crystals with interesting optical properties can be made by "steering" the crystallization process. Such colloids can be used to confine, switch, and amplify light in optoelectronic devices. One technique used by Velikov *et al.* is to grow the crystals on patterned templates. A second trick is to use the capillary forces exerted by a drying front to force small colloidal particles into the holes between the larger ones.

With these techniques, the authors obtain very large single crystals of structures, such as the peculiar LS$_3$ structure, which will not form in bulk colloidal crystallization. This holds especially for the crystals that were obtained by making a binary crystal of two different colloids, one of which can be burned away. What remains is a low-density crystal of the heat-resistant colloid. This crystal could never have formed by spontaneous self-assembly. The report by Velikov *et al.* illustrates that completely novel colloidal materials can be made by combining the use of tailor-made building blocks with novel construction methods.

Pham *et al.* (*2*) address another long-standing question: What would happen to the phase behavior of spherical particles if we could change the range of attraction? In simple atomic systems, this question cannot be addressed because the range of the attractive forces depends only on fundamental physical constants, and these cannot be changed. For this reason, Van der Waals's law of corresponding states holds for all simple molecules. However, in 1983 Gast *et al.* (*9*) showed that the law of corresponding states does not hold for colloids with short-ranged attraction. These suspensions have only two phases: fluid and solid. The colloidal liquid-vapor transition has disappeared.

Pham *et al.* studied the effect of short-ranged attractions on glass formation. In the glassy state, the system is out of equilibrium—the equilibrium state would be a crystal. However, hard-core colloids can be made to bypass crystallization and form a dense glassy state (*10*). In this glass, the colloids are unable to diffuse because they are confined in the cages formed by their neighbors. Switching on an attraction between colloids in the glassy state makes them stick together. One might think that this would make it even harder for the colloids to move.

Not so, say Pham *et al.* Initially, the effect of attraction is to break up the glassy structure. This is surprising: it is like loosening up a packed bed of glass beads by adding glue. When the attraction is made sufficiently strong, the system again forms a glass. But now the colloids are not confined due to repulsion but rather due to attraction (see the figure). Theoretical work by Dawson *et al.* (*11*) and by Pham *et al.* suggests that, when the strength of the attraction is increased, there can be a sharp transition from the repulsive to the attractive glass. In the equilibrium crystal phase, computer simulations have shown that short-ranged attractions can cause a first-order phase transition from a repulsive to an attractive solid (*12*). But the nature of the transition between nonequilibrium repulsive and attractive glasses is not clear. Future experiments will have to reveal how the colloidal glass behaves in the vicinity of this transition.

Insights into the nature of "attractive" and "repulsive" colloidal glasses should improve our understanding of glasses and gels formed by smaller molecules, such as globular proteins. In particular, it would be interesting to know whether nature employs similar tricks to control the mechanical properties of gels in living organisms.

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PERSPECTIVES: POLYCRYSTALLINE MATERIALS

Grain Boundaries and Dislocations

Helena Van Swygenhoven

In coarse-grained metals, plastic deformation is mainly carried by dislocations—line defects of the regular crystal lattice—within the individual grains. Dislocations can move through the crystal grains and can interact with each other (*1*). Grain boundaries often hinder their transmission, creating a dislocation pile-up at the boundary and thereby making the material harder to deform.

One of the best known theories based on dislocation pile-up, described by the Hall-Petch equation (*2*, *3*), predicts the hardness of the material to be inversely proportional to the square root of the grain size. However, as grain sizes are reduced to the nanometer scale and the percentage of grain boundary atoms increases correspondingly, this traditional view of dislocation-driven plasticity in polycrystalline metals needs to be reconsidered. In a sample with grain diameters of 20 nm, 10% of atoms are located at grain boundaries. Dislocation sources and pile-up are hardly expected to exist in such a material and deformation is believed to be carried mostly by the grain boundaries via a particular accommodation mechanism.

Experimental measurements have shown various deviations from the Hall-Petch equation as grain sizes reach the nanometer scale. Some may be attributed to synthesis or measurement artifacts; others indicate intrinsic properties of the nanostructured materials (*4*, *5*). However, atomic level understanding of the grain boundary accommodation mechanism is limited. No direct experimental visualization technique is available that allows nonintrusive investigation of grain boundary structures during deformation. Transmission electron microscopy requires samples to be thinned to a thickness comparable to the grain size, inducing structural relaxations and thus changing the grain boundary structure (*6*).

Massively parallel supercomputers offer the possibility to shed light on the deformation mechanism in atomistic simulations involving millions of atoms, equivalent to computer samples of three-dimensional networks of up to 15 grains with a 20 nm diameter or 100 grains with a 10 nm diameter (see the figure). When a special replica technique known as periodic boundary conditions is used, the sample can be considered as a small part of an infinitely large bulk nanocrystalline sample.

The computational sample may be "synthesized" in different ways, such as cooling down from the melt, compaction of nanoclusters, and a simple space-filling technique called the Voronoi construction (*7*–*9*). These techniques lead to the formation of different grain boundary structures. For example, liquid-like grain boundaries can result from cooling down from the melt, whereas grain boundaries with a high degree of structural order, not fundamentally different from the grain boundaries in

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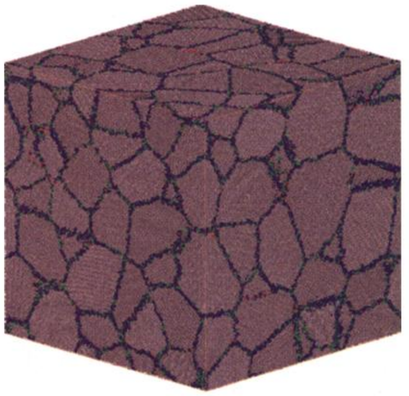
polycrystals, are obtained when a Voronoi construction is used. Thus, the first important task in a simulation is to produce nanostructures that resemble closely what is experimentally synthesized.

Most computer simulations have been performed on face-centered cubic metals. Large-scale molecular dynamics simulations have provided evidence for a transition, with increasing grain size, from intergranular plastic deformation based on grain boundary accommodation, to a mixture of intergranular and intragranular processes where the grain boundary acts as a source of imperfect or partial dislocations (*10–12*).



Grain boundaries at the nanoscale. Computer-simulated sample of nanocrystalline Ni with a mean grain diameter of 10 nm. Each side of the box is 37 nm long, and the sample contains 4.6 million atoms. Gray atoms sit in perfect crystalline positions; colored atoms are grain boundary atoms.

At the smallest grain sizes, room temperature simulations on samples with randomly distributed grains and grain orientations identified grain boundary sliding as the accommodation mechanism. The sliding is triggered by uncorrelated shuffling and to some extent by stress-assisted diffusion (*13*). On the other hand, simulations at higher temperatures on samples with symmetric grains and only high-energy grain boundaries, suggest that sliding is governed by enhanced grain boundary diffusion ("Coble creep") (*14*). The authors extrapolate Coble creep to room temperatures, on the basis of the presence of highly disordered grain boundaries. There is, however, no real justification for such an extrapolation, because it cannot be assumed that the rate-limiting process near the melting temperature also dominates at room temperature.

For larger grains (but still in the nanometer scale), grain boundary accommodation remains dominant, but grain boundaries start to also emit partial dislocations. As grain sizes increase, several partial or imperfect dislocations nucleate in different regions of the grain boundary, in contrast to the emission of full or perfect dislocations known from coarse grained metals (*15*).

Recently, full dislocations have been observed in simulations of columnar microstructures with grain sizes of 30 nm; plasticity was fully determined by dislocation activity (*16*). These samples are essentially two-dimensional, however, with only two slip planes for dislocations allowed. The energetics of a two-dimensional, infinitely extended dislocation structure are different from those of a full dislocation where the core line is pinned at both ends to a general grain boundary, and therefore the results cannot be compared.

Atomistic simulations of deformation are performed under high stresses and during very short deformation times (around 150 ps). It is often claimed that a steady-state strain rate is reached, justifying the calculation of activation energies. But this "steady state" is time-dependent. A reduction in strain rate by a factor of 10 has been observed when the simulation time was increased from 150 ps to 1 ns, a time still much shorter than in experiments. The rate-limiting processes addressed in these calculations are thus very dependent on the initial grain boundary structure and the loading conditions. During longer deformation times, many other processes take place in the grain boundary that change its structure during deformation. At room temperature, grain boundary structural relaxations toward lower energy structures have been observed, whereas at high temperatures, enhanced melting is to be expected.

Despite their limitations, the insight provided by simulations at the atomic scale is invaluable for guiding and understanding experimental results and for developing new theories. The future lies in a better understanding of the relation between grain boundary structures and their behavior under stress. Detailed knowledge of the relation between grain boundary structure and its mechanical behavior will allow the design of sophisticated microstructures and will lead to synthesis methods that produce improved grain boundary structures.

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PERSPECTIVES: PALEOCLIMATE

Trans-Atlantic Climate Connections

Paul A. Baker

Modern climate studies are limited by the short duration of instrumental records, particularly in the tropics. Modes of climate variability with periods greater than a few decades are only partially known and not well understood (*1*). If we are to understand tropical climate variability at longer time scales, we have to rely on proxy records such as those contained in lake sediments, reef corals, or high-altitude ice cores.

Several recent articles have sharpened the focus on the past and present climate of the tropics. On page 113 of this issue, Johnson *et al.* (*2*) describe a new sedimentary record spanning the past 25,000 years from Lake Malawi, one of the great lakes of tropical East Africa. Their discussion centers on finely-resolved biogenic silica in the record, a possible indicator of past precipitation. But equally impressive is their use of Nb/Ti as a fingerprint for volcanic ash, and benthic diatoms for reconstruction of past lake levels.

Disregarding as possible artifacts those silica peaks that coincide with the two Holocene ash events, two distinctive long-term climatic phases stand out. Low silica accumulation coincides with low lake level between 25,000 and 16,000 years before present (yr B.P.) and, again, between 13,000 and 11,000 yr B.P. After 11,000 years B.P., lake level and silica both increased to values maintained to the present.

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